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Project Summary

Characterization of Scrubbed and Unscrubbed Power Plant Plumes

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Airborne measurements of scrubbed and unscrubbed plumes from the Widows Creek Steam Plant were made during August 17 to 25, 1978, under the SCRUB program. Data from the flight program (except size distribution data) and preliminary data analysis results have been previously published in a Data Volume.

This report briefly describes the flight program and methodology of SCRUB and gives an analysis of the data gathered. The results cover plume chemistry, primary aerosol, aerosol size distributions, and aerosol formation rates among the scrubbed and mixed plumes.

Little difference was seen in photochemical aerosol and sulfate formation in the scrubbed and unscrubbed plumes. However, measurement noise and plume mixing may have obscured moderate differences. The submicron primary emissions from the scrubbed unit were only about 14 percent of those from the unscrubbed unit.

Sulfur dioxide to sulfate conversion rates in the plumes were between 0 and 3.2 percent per hour. Aerosol formation rates varied between 0 and 0.30 microns^3/(ppb SO_2 - hr - cm^3). More sulfate was measured than could be accounted for by the aerosol measurements.

Ozone bulges of 40 ppb were typical in the afternoon 50 kilometers downwind of the plant.

Photochemical reactions were most rapid when the plume was dilute and the sunlight strong.

Submicron primary emissions from all units appeared to be mostly sulfuric acid.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The production of primary and secondary pollutants has been studied extensively in the plumes of unscrubbed power plants, but little work has been done to study the effects of wet scrubbers on downwind plume chemistry. The environmental laws coupled with the cost of low sulfur coal are such that the installation of SO_2 wet scrubbers are certain to become more common in the future. Therefore, it is necessary to obtain information on any possible adverse effects from using wet scrubbers to control SO_2 emissions from utility boilers.

A number of studies have been conducted to establish gas to particle conversion rates in urban and in conventional power plant plumes. These studies indicate conversion rates

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for SO_2 to sulfate aerosols of between 0 and 10 percent per hour.

One of the principal pathways leading to sulfate formation in the atmosphere is the SO_2 + OH radical reaction. Since the hydroxyl radical is formed photochemically, the conversion rate should depend on the amount of solar radiation.

SO_2 oxidation may also take place on the surface of existing particles or in water droplets. This liquid phase oxidation may play an important role under high humidity conditions or in moisture laden power plant plumes. Thus, the SO_2 conversion rate may be affected by the droplets produced by a wet scrubber on a power plant.

The purpose of the study was to investigate the SO_2 conversion rate in the plume and to determine if it differed significantly from that found in unscrubbed power plant plumes.

Experimental Approach

The Tennessee Valley Authority Widows Creek Steam Station near Stevenson, Alabama, was studied in this project. The plant's six 135 MW units (Units 1-6) are connected to a single 1000 foot stack. Two additional 557 MW units have individual 500 foot stacks and electrostatic precipitators of 90% efficiency. Unit 8 is equipped with a combined venturi and limestone wet scrubber having a design efficiency of 80% for SO_2 removal. The effective particulate removal efficiency for Unit 8 is 99.5% by weight. Ammonia (about 10 ppm) is added to the Unit 7 flue gas to increase the particulate collection efficiency. Units 1-6 burn 1 percent sulfur coal; Units 7 and 8 burn 4 percent sulfur coal.

The field study involved sampling in the power plant plume using a Beechcraft Queen Air fixed wing airplane to carry the sampling equipment. The sampling and monitoring equipment is listed in Table 1.

Three types of flight maneuvers were used in the program: traverses, spirals, and orbits. Traverses gave horizontal distributions of measured parameters. Spirals gave vertical distributions of the important species. Orbits were performed to obtain filter or impactor samples at a specific location.

To produce plume cross sectional plots, the data from the traverses were plotted in cross sections with the endpoints of each traverse fixing the traverse line. Contours were then drawn. Since completing a traverse requires 15 to 60 minutes, these cross sections give true plume concentrations only for steady state situations.

Table 1. Queen Air Instrumentation

Parameter	Manufacturer/Model	Analysis Technique
SO_2	Meloy 285	Flame Photometric
NO/NO_x	Monitor Labs 8440	Chemiluminescence
O_3	CSI	Chemiluminescence
Sulfate	MRI Two-Mass	Flash vaporization/flame photometric
	ERT RSP sampler	Ion Chromatography
Light Scattering	MRI 1550 MRI 1569	Integrating nephelometer
Condensation Nuclei	Environment One Rich 100	Light Attenuation
Turbulence	MRI 1120	Pressure Fluctuations
Temperature	YSI/MRI	Bead Thermistor
Elemental Analysis	Lundgren 4-stage Impactor	Analysis by PIXE
Dew Point	Cambridge Systems 137	Cooled Mirror
Altitude	Validyne	Absolute Pressure Transducer
Airspeed	Validyne	Differential Pressure Transducer
Position	King KX170B/HTI DVOR	Aircraft DME/VOR
Aerosol Charge Acceptance	Washington U.	Aerosol Charge Acceptance
Data Logger	MRI Data System	9-Track Tape - 6 hr.Capacity
Stripchart Recorder	Linear Instruments	Dual channel
Particulate Sulfur	Meloy 285	Upstream SO_2 Scrubber/ Measurement of Total Sulfur
Aerosol Size Distribution	TSI 3030	Charger/Mobility Analysis
Aerosol Size Distribution	Royco 218	Optical Particle Counter
Aerosol Size Distribution	Knollenberg ASSP	Axial Scattering Spectrometry

A total of ten flights were flown during August 17-25, 1978. All data collected are available in a Data Volume and on magnetic tape. Several flights provided studies of the scrubbed and unscrubbed plumes. On August 17 and 23, Unit 7, the largest unscrubbed unit, was not operating; flights on those days gave data on the scrubbed and mixed plumes. On August 19, morning and afternoon flights were made while all units were operating.

The weather varied little during the study period. The days were clear and the plume well mixed by 10 or 11 a.m. each day. A moderate to strong inversion formed each night and broke up by 9 a.m. the following morning. Winds were moderate at plume elevation, typically 10-15 km/hr.

Results and Discussion

Photochemical aerosol formation in the plume was calculated in two ways: (1) using sulfate concentration determined from filter samples and (2) using aerosol size distributions measured with the electrical aerosol analyzer (EAA) and the bag sampling system. The sulfate results are discussed, then the EAA, and finally a comparison is made between the two techniques.

Sulfate Measurements

Three methods were used to determine sulfate concentrations. Sulfate in the Lundgren impactor samples was measured as total sulfur by proton induced X-Ray Emission. The sulfur values on the impactor filter and last stage were added together to give the sulfur in particles less than one micron in size. Sulfate on the Two Mass filter

was measured by flash vaporization followed by flame photometric analysis. Sulfate on the Teflon™ coated glass fiber filters was extracted with water and measured by ion chromatography.

Of the three methods the IC analysis of the Teflon™ coated filters was judged to be the most accurate because of its simplicity and because the technique was unlikely to introduce errors. Pairwise comparisons among the three data sets showed good correlation (r^2=0.74) between the flash vaporization/FPD and the IC values. Other correlations were not very good. In all data analysis the FPD values were used since they correlated well with the IC results and since many more FPD samples were available than IC ones.

Table 2 shows the sulfate formation rates obtained using the FPD data.

The data set exhibits significant scatter, i.e., some excessively large sulfate numbers and several negative values, which are physically unrealistic. As an entity, the data appear to be reasonable and generally consistent with results from other studies showing 0-10% hr^{-1} conversion rates of SO_2 to sulfate aerosol.

Aerosol Formation

Aerosol formation rates were calculated using the EAA size distribution data. The data are shown in Table 3. The plume excess aerosol volume has been divided by the SO_2 concentration to reduce the impact of plume dilution in the comparison. Plume excess volumes, $\bar{V}_{pe}$ were calculated using the following equation: $\bar{V}_{pe} = \bar{V}_p - \bar{V}_B - \bar{SO}_2(\bar{V}^*/\bar{SO}2^*)$ where $\bar{V}_p$ and $\bar{SO}_2$ are the average aerosol volume and SO_2 concentration in the plume at a given distance, V_B is the average aerosol concentration in the background air, and $\bar{V}^*/\bar{SO}2^*$ is the ratio of primary source aerosol concentration to SO_2 concentration obtained from measurements close to the source.

Table 3 shows that aerosol formation did not occur significantly near the source or early in the morning even on sunny days. Maximum rates were observed near noon or in the early afternoon.

The SO_2 conversion to aerosol was of interest in these calculations. Using the EAA data, the SO_2 conversion rate is the normalized volume formation rate times a constant, Cs, which depends on the aerosol composition. The following assumptions were made: (1) the sulfuric acid formed by SO_2 oxidation was

Table 2. In Plume Sulfate Formation Based on Filter Measurements

Date	Sample Times	Distance (km)	Sulfur Conversion Rates (%/hr) From Start	Sulfur Conversion Rates (%/hr) From Previous Distance
8/17	Morning			
	0853-0933	0.5	n.a	
	1024-1116	3	n.a.	
	1129-1159	9		
8/17	Afternoon			
	1551-1635	0.5	n.a.	
	1732-1805	3.0[1]	n.a.	
	1821-1852	7.0		
8/17	Average			
	0853-1852	<9	n.a.	
8/19	Early Morning			
	0717-0736	0.5	n.a.	
	0756-0826	9	n.a.	
	0845-0944	24	0.6	0.4
	0917-0932	25	0.4	<0
	0955-1007	45	1.4	2.7
	1011-1026	47	1.1	1.6
	1038-1053	75	1.3	1.4
8/19	Average			
	0717-0826	<9		
	0955-1053	45-75	1.3±0.1	1.9±0.4
8/19	Afternoon			
	1407-1424	58	2.1	
	1516-1529	0.5		
	1553-1618	9-13	6.8[2]	
8/21	Morning			
	0734-0844	15-20	0.2	
	0857-0925	30	.8	
	0936-1031	15	0.4	
	0949-0959	20		
8/21	Average			
	0734-1031	15-30	0.5±0.2	
8/23	Morning			
	0944-0950	11-14		
	1134-1231	50		
	1252-1259	50		
8/23	Afternoon			
	1441-1531	70	0.7	
	1710-1719	50		
	1822-1828	13		
8/25	Morning			
	0543-0645	0.5	n.a.	
	0652-0736	0.5	n.a.	
	0830-0845	20		
	0857-0912	8		
8/25	Average			
	0543-0912			
8/25	Late Morning			
	1053-1108	45	0.6	
	1240-1255	50	2.9	
	1301-1316	45	3.2	
8/25	Average			
	1240-1316	47.5	3.0±0.2	

[1] *May be left over plume, travel time very uncertain.* [2] *Number unreliable.*
n.a. - not applicable

Table 3. Aerosol Growth Rate Calculations

Date	Time	Distance (km)	Excess Plume Vol./ SO_2	Aerosol Growth Rate/ppb SO_2 $\mu m^3/(cm^3$-ppb-h) From Start	From Previous Distance	Percent/Hour Conversion From Start	From Previous Distance
8/17	Morning						
	1024-1115	3	<0				
	1128-1158	9	<0				
8/17	Late Afternoon						
	1732-1751	3	0.055*	0.13		1.2	
8/19	Early Morning						
	0759-0825	9	<0				
	0847-0907	24	<0				
	0916-0926	24	<0				
	0956-1005	45	<0				
	1018-1023	45	0.009	0.003	0.013	0.02	0.12
	1039-1050	75	0.083	0.016	0.044	0.15	0.40
8/19	Afternoon						
	1412-1415	58	0.19	0.04		0.37	
8/21	Morning						
	0811-0839	15	0.000				
	0908-0921	30	0.016	0.009	0.023	0.09	0.20
	0937-1029	17.5	0.050**	0.036**		0.32**	
8/23	Morning						
	1024-1041	11-14	0.023	0.026		0.24	
	1134-1236	50	0.28	0.078	0.095	0.72	0.88
8/23	Afternoon						
	1450-1526	70	1.67	0.26		2.4	
	1714-1723	50	1.15	0.24		2.2	
	1836-1845	13	0.009	0.006		0.059	
8/25	Early Morning						
	0544-0735	0.5	0.000				
	0833	20	0.009	0.010		0.010	
	0902	8	<30				
8/25	Late Morning						
	1055-1106	45	0.078	0.022		0.20	
	1135-1138	45	0.131	0.037		0.34	
	1311-1314	45	0.26	0.093		0.85	
	1242-1252	50	0.84	0.30		2.8	

**May be left over plume, travel time very uncertain.*
***Poor background data (used 30 km background).*

neutralized by ammonia and (2) the relative humidities observed during the study (usually 60 to 80%) caused the ammonium sulfate to deliquesce. Under these assumptions the aerosol was about 45% by weight ammonium sulfate; the Cs value was 0.092, with units ppb SO_2 equivalent per ($\mu m^3/cm^3$). The sulfate formation rates calculated from these data can then be compared to those determined from the filter data.

Comparison of Sulfate and Aerosol Formation Rates

The sulfate and aerosol formation results should be related because most of the sulfate will be found in the small (0.1-1.0μ) aerosol particles measured by the EAA. One would expect the aerosol volume calculations to be lower than those measured by the EAA because compounds other than ammonium sulfate and water are likely to be in the aerosol phase.

Table 4 compares the plume excess aerosol volume measured by the EAA and that calculated from the plume excess sulfate data using the filter values. Before forming the ratios in Table 4 the plume excess aerosol concentrations were normalized by the average SO_2 concentration at the measurement points and the plume excess sulfate concentrations were normalized by the average SO_2 concentration during the filter sampling periods.

Table 4 shows that much more sulfate was seen by the filter measurements than can be accounted for by the EAA data. One would expect the reverse as discussed previously. There is no ready explanation for this. Possible factors which may have contributed to the discrepancy include: (1) Sampling bias—sulfate usually forms more rapidly when the plume is dilute. Since the filter samples are averaged across the entire plume and the EAA data are taken from a 4-second grab sample, the filter may have collected higher sulfate values. (2) Aerosol hydration—under drier conditions ammonium sulfate would be present as a solid particle instead of as a deliquesced droplet, assuming a dry aerosol would reduce the ratios in the table by a factor of 2.5. (3) Bias in Sulfur Measurements—the IC data showed significantly more sulfate than the Two Mass data, which was used in these calculations. The Two Mass data set seems more likely to be biased low than the IC data to be biased high. If the Two Mass data are correct, the ratios would be reduced by a factor of 1.5. However, the sulfur conversion rates as calculated are reasonable in comparison with previous studies. (4) EAA Bias—EAA measures the total volume with about 30 percent accuracy. It will usually overpredict concentrations in the last two measurement channels. In these calculations data from the last channel were excluded because of excessive instrument noise. The exclusion of these factors may have resulted in a lowering of the EAA data by a factor of about 1.2.

A combination of the above errors could account for the high sulfate to aerosol ratios in Table 4, but there is no adequate evidence to point to any of them.

Conclusions and Recommendations

The principal conclusion from the study was that no significant increase in sulfate formation was caused by the presence of the wet scrubber. Aerosol formation rates were nearly identical when Unit 7 (unscrubbed) was and was not operating, although measurement noise could possibly affect the values by a factor of two. Photochemical activity,

Table 4. Comparison of Sulfate and Aerosol Measurements

Sample Time	Distance (km)	Sulfate As* Aerosol Volume / Measured Aerosol* Volume by EAA
8/17 Morning	0.5	3.8
	3	3.1
	9	5.4
8/17 Late Afternoon	0.5	0
	3	2
	7	30
8/19 Early Morning	0.5	0.58
	9	2.3
	24	4.6
	25	3.3
	45	16
	47	9.1
	75	8.8
8/19 Late Afternoon	9-13	58
	58	4.3
8/21 Morning	15-20	4.1
	15	0.9
	20	<0
	30	1.7
8/23 Morning	11-14	16
	50	-0.2
8/23 Afternoon	13	1.1
	50	24
	70	6.7
8/25 Early Morning	0.5	0.58
	0.5	8.4
	8	<0
	20	<0
8/25 Late Morning	45	3.9
	45	0.50
	50	1.2

**Plume excess including primary emissions.*

indicated by ozone formation in the plume, was observed about 50 km downwind on occasions when Unit 7 was and was not operating. The ozone formation in the plume was more a factor of solar insolation and plume mixing with background air than of the presence or absence of the scrubbed or unscrubbed plume. The maximum aerosol formation was measured for downwind (40 km or more) when the plume was well mixed and sunlight was strong. When expressed as pseudo first order sulfur conversion rates, average aerosol formation rates of 2.5 percent per hour were typical between 10 am and 5 pm. The aerosol concentrations predicted from the plume excess sulfate measurements were usually about 3 times higher than the measured concentrations; this large disagreement probably has more than one cause. No useful nitrate formation data were obtained because the amount of nitrate collected on the filters was near the blank values. Observations of NO_x removal from the plume indicate an afternoon removal rate of 25 percent per hour, a value much higher than for SO_2.

The results of the study indicate several lines of future research. Specific recommendations include:

1. The large difference between the sulfate and aerosol measurements should be resolved, possibly by comparing b_{scat} measurements with the sulfate and aerosol data.
2. The near source aerosol formation rates should be investigated, possibly by computing changes in nuclei mode particle concentrations.
3. The EAA data should be better corrected for altitude and channel cross sensitivity. This adjustment might improve the estimates of the aerosol formation rates. The inverted data may then be analyzed to establish the relative contributions of gas and liquid phase chemical reactions to aerosol formation.

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The complete report, entitled "Characterization of Scrubbed and Unscrubbed Power Plant Plumes," was authored by G. R. Markowski, J. L. Stith, and L. Richards of Meteorology Research, Inc., Santa Rosa, CA 95401 (Order No. PB 82-101 346; Cost: $8.00, subject to change) will be available only from:

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